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EVALUATION OF NEW BRUNSWICK LIMESTONE AS SO_2 SORBENTS IN FLUIDIZED BED COMBUSTORS

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EVALUATION OF NEW BRUNSWICK LIMESTONES AS SO2 SORBENTS IN FLUIDIZED BED COMBUSTORS

by

C.A. Hamer*

ABSTRACT

Ten limestone and one dolomite sample from eight deposits in New Brunswick were evaluated in a bench-scale fluidiized bed reactor to determine their performance as SO2 sorbents in fluidized bed combustors. Six of the samples were tested in six particle size fractions. Sulphation capacity increased with decreasing particle size. The sulphation capacity determined from the chemical analysis of the sulphated rock was higher than that calculated from the fluidized bed reactor results. A sample of marl, with an average particle size of 44 um, was evaluated in a pilot-scale circulating fluidized bed unit. It achieved 80 % sulphur retention at Ca/S = 1.75.

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ÉVALUATION DES PROPRIÉTÉS DU CALCAIRE DU NOUVEAU-BRUNSWICK COMME PRODUITS DE SORPTION SO_2 DANS LES FOURS À LIT FLUIDISÉ

par

C.A. Hamer*

RÉSUMÉ

On a évalué dans un réacteur à lit fluidisé expérimental, dix échantillons de calcaire et un échantillon de dolomie provenant de huit gisements du Nouveau-Brunswick, dans le but de déterminer leur performance comme produits de sorption SO_2 dans des fours à lit fluidisé. On a fait des essais avec six échantillons divisés en six fractions granulométriques. La capacité de sulfatation a augmenté avec la diminution des particules. De plus, la capacité de sulfatation déterminée à partir d'analyses chimiques était plus grande que celle calculée à l'aide des résultats d'essais dans le réacteur à lit fluidisé. Enfin, un échantillon de marne, d'une granulométrie moyenne de 44 µm, a été évalué dans une installation pilote à lit fluidisé circulant. Les résultats d'essais ont indiqué une capture du soufre de 80 % à CA/S = 1,75.

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INTRODUCTION

Limestones and dolomites are used as SO2 sorbents in fluidized bed combustors. This report is an evaluation of eight limestones, one of which is actually a marl, and one dolomite from New Brunswick for their utilization as SO2 sorbents in fluidized bed combustors. The initial samples from five deposits were obtained in 1981 and the latter samples from seven deposits, some of which were repeats from the original five, were collected in 1986. The early work (1) was part of a general study on limestones with emphasis on atmospheric bubbling fluidized beds (AFBC). This present study is principally directed towards evaluating sorbents for the Chatham circulating fluidized bed combustor (CFBC).

Limestones from different sources may differ in their reactivity to SO2 and ability to capture that gas. The efficiency of the limestone as an SO2 sorbent is dependent upon the physical and chemical composition of the rock. The sulphation reaction: $CaO + SO2 + 1/2\ O2 = CaSO4$ takes place at the surface and in the pores of the sorbent material. As the molar volume of CaSO4 is considerably greater than that of CaO or CaCO3, the reaction product coats the surface and blocks the pores. Consequently the more porous the limestone and the smaller the particle size, the greater will be the sulphation capacity.

There are two types of atmospheric fluidized bed combustors: the bubbling bed and the circulating bed. The former utilizes limestone in the particle size range 3-0.5mm, whereas the latter uses material of -1mm or smaller. The efficiency of sorbent utilization is much greater in the circulating FBC primarily due to the finer sorbent particle size. However, if the material is very small, less than approximately 50 um, it may be elutriated from the FBC rather than recycled to the combustor by the cyclone, thus reducing the overall utilzation of the limestone.

The most practical method of evaluating the efficiency of a limestone as a sorbent, other than a full-scale test, is by thermogravimetric analysis (TGA) or in a bench-scale fluidized bed reactor (FBR). The latter more closely approximates the actual conditions to which limestone is exposed in an FBC, that is, thermal shock, simultaneous calcination and sulphation and attrition. For testing fine particles which may be elutriated from a fluid bed, the TGA method may be more practical. To evaluate sorbent behaviour for use in a bubbling FBC, limestone particles are tested in size range 1.00 - 0.841 mm. Because the particle size distribution is smaller for the limestone used in a circulating FBC, it is necessary to pelletize the finer sizes of this material to prevent its eleutriation from the fluidized bed test reactor. This method permits a reasonably accurate ranking of a series of limestones. It is however not possible to use this FBR data to model predicted sorbent requirements for a CFBC.

SORBENT SAMPLES

Source

The initial samples of NB sorbents, NB-2 to NB-5, were supplied by D.E. Barnett, New Brunswick Dept of Natural Resources, in 1981. The series NB-1 to NB-1-13 are all from Havelock Lime Works. They represent samples from two quarries: the Samphill quarry and the Canada Cement quarry at Havelock, collected since 1980. Only the last two samples from Havelock supplied in 1986 by New Brunswick Electric Power Corpoation (NBEPC) will be included in this report. The remaining samples were supplied by NBEPC.

Table 1. New Brunswick Sorbents

NB-1-12	Limestone from Havelock Lime Works Samphill quarry, supplied by NBEPC Jan 1986
NB-1-13	Limestone from Canada Cement quarry at Havelock, supplied by NBEPC Jan 1986
NB-2	Limestone from a quarry at Carlisle, Carleton County, 1981
NB-3	Dolomite from Brookville Manufacturing Co. Ltd., quarry, Brookville, Kings County, 1981
NB-4	Limestone from Elmtree Resources quarry, near Petit Rocher, Gloucester County, 1981
NB-4-2	Limestone, (Ag Lime), from Elmtree Resources, Elmtree quarry, supplied by NBEPC Feb 1986
NB4-3	Limestone from Elmtree Resouces, Sormony quarry, also by NBEPC
NB-5	Limestone from a quarry at Windsor, Carleton County, 1981
NB-6	Limestone from Glebe Mine (ore dump near old shaft), supplied by NBEPC Jan 1986
NB-7	Limestone from Markhamville #2 Shaft, supplied by NBEPC Jan 1986
NB-8	Marl from drained lake bed, Upper Kent, Carleton County, supplied by NBEPC, June 1986

Sample Preparation

Samples received were of various size and quantity. Rock was reduced to the desired size in a jaw crusher, gyratory cone crushers and a disc pulverizer. A representative sample was taken for chemical analysis. The material was sieved to provide the 0.841-1.000 mm size standard for all tests. The 1986 samples were sieved to give a complete series of size fractions as follows in Table 2.

Table 2. Size range of limestone samples

Tyler Mesh	metric opening	average
16*20	1.00 mm * 850 um	925 um
20*28	850 um * 595	722
28*48	595 * 300	448
48*65	300 * 212	256
65*100	212 * 150	181
100*200	150 * 75	113
200*325	75 * 45	60

The 595*300 um sample and those of finer particle sizes were blended with bentonite, in an amount of 2 mass %, and agglomerated on a disc pelletizer. The pellets were dried and sieved to 1400*850 um for testing. Agglomeration of the fine material was necessary to prevent its eleutriation from the bed by the fluidizing gas.

The marl sample, NB-8, was collected from a drained lake bed. As received, it contained 35% moisture. The marl is a very fine, light grey, powdery material. The sample contained some 1 to 3 cm rocks and small pieces of wood as well as fine strands of vegatation (peat?). The size analysis by a Leeds and Northrup Microtrack Particle Analyser gave an average particle size of 44 um. Upon drying the sample in pans over a steam heater, most of the material remained agglomerated as -2 cm pellets. These had sufficient strength that they generally remained intact upon dropping from about 1 m onto the floor. However, they could be easily crushed with a rolling pin. Samples were tested as "natural" pellets and also agglomerated into pellets with bentonite binder.

Sample Composition

The calcium, and when analysed, the magnesium, content of the sorbent samples are given in Table 3.

Table 3. Carbonate analysis of New Brunswick sorbents

Sample		$CaCO_3$	$MgCO_3$
NB-1-12	Samphill	97.2	-
NB-1-13	Havelock	97.6	-
NB-2	Carlisle	98.4	1.0
NB-3	Brookville	54.1	45.0
NB-4	Elmtree	91.5	1.0
NB-4-2	"	96.4	-
NB-4-3	" Sormony	93.8	-
NB-5	Windsor	97.6	1.6
NB-6	Glebe Mine	96.5	-
NB-7	Markhamville	95.9	-
NB-8	Upper Kent	88.6	-

Sulphation Tests - Fluidized Bed Reactor

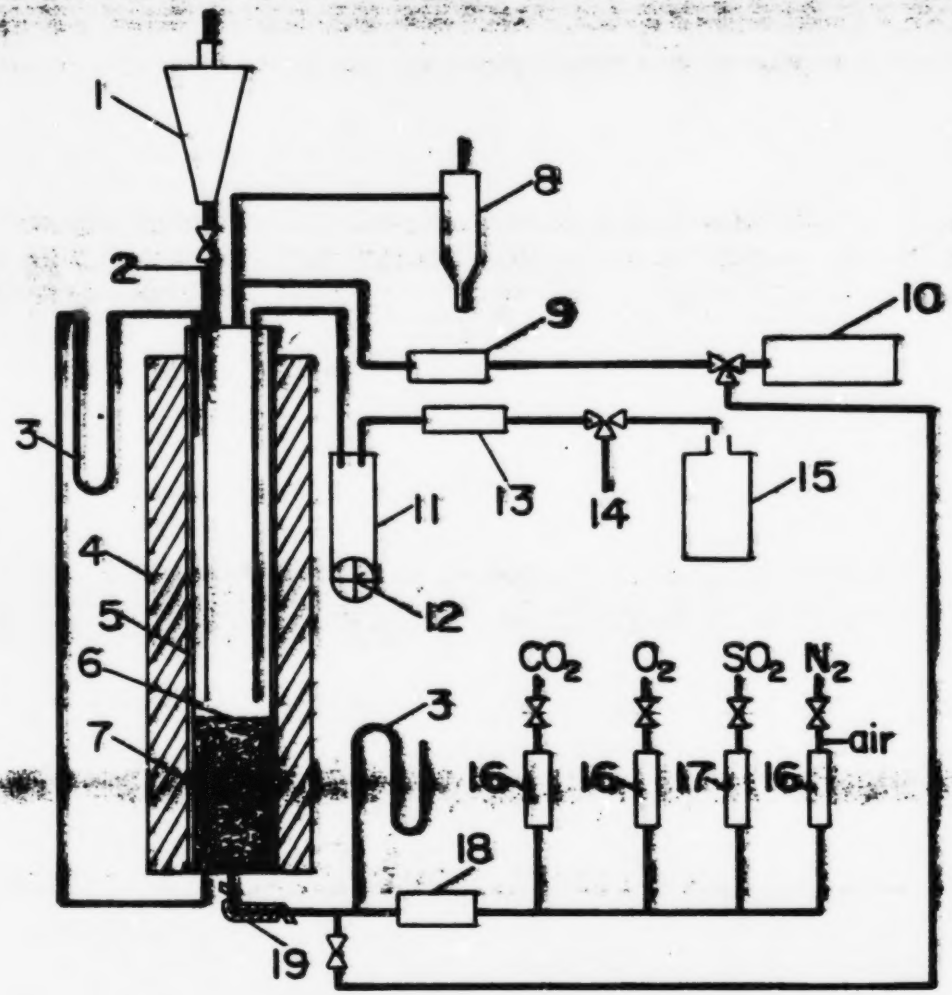
Sulphation tests were conducted in a bench-scale fluidized bed reactor (Fig 1). Although the limestone evaluation method with the FBR has been previously reported elsewhere (1), a brief description is given here. The reactor is an externally heated stainless steel pipe, 53 mm dia by 1400 mm high, with a porous silica disc as a distributor located 350 mm from the bottom. For each test the reactor, with a bed of 250 g ASTM C109 silica sand fluidized by nitrogen was heated to 850 C. Then the synthetic flue gas, 0.26 % SO2, 8 % CO2, 5 % O2, balance N2, was admitted to the reactor. Ten grams of limestone rock or pellets were injected into the fluidized bed. The SO2 in the exhaust gas was continuously analysed by a Beckman Infrared Analyser. Within a minute of adding the sample the SO2 concentration in the exit gas dropped to a fraction of the inlet concentration. It then began to increase, the rate of increase being dependant upon the sulphation characteristics of the limestone, until after one to three hours the exhaust concentration was constant at or very near to the inlet concentration. As the area above this curve represents the SO2 captured by the sorbent it is possible to calculate the percent sulphation versus time for the sample.

A standard limestone is periodically tested during a series of runs to ensure the consistancy of the method.

Pilot-scale Circulating Fluidiized Bed

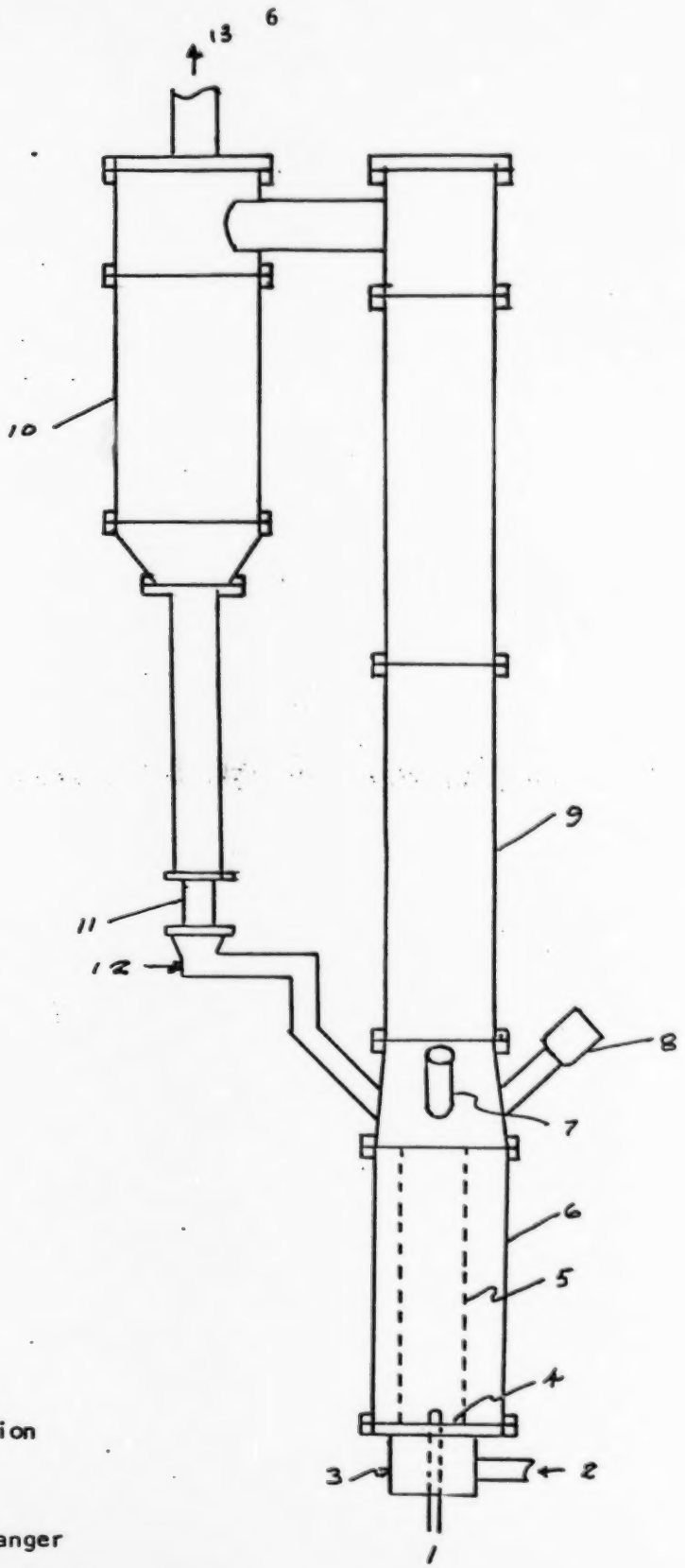
A pilot-scale CFBC was used to evaluate the marl sample from Upper Kent, NB-8. This CFBC test unit, shown in Fig 2, consists of three main parts; the 152 mm (6 in.) dia. dense bed section, the 100 mm (4 in.) dia. combustor column and the high temperature cyclone with hot solids return leg. The smooth changeover of the diameter is given by the transition section. The dense bed section is simply a length of stainless steel pipe (6 in., Sch.40), while all the combustor sections are made from 100 mm i.d. ceramic tubes cast with insulating refractory inside a steel shell. The sections are bolted together by means of flanges. The overall height of the combustor is 2.81 m. The entire combustor is suspended from the ceiling of the laboratory. This type of support allows the combustor to expand freely when being heated and easy access to all parts of the combustor.

The combustor is heated electrically around the dense bed section and also by a propane burner in the transition section for startup. The sorbent and fuel, in this case, Syncrude byproduct fluid coke, were blended and fed pneumatically from a fluidized bed feeder. Because byproduct coke is a very unreactive fuel, the initial heat up was aided by over-bed feeding of a sub-bituminous coal. A water-cooled heat exchanger followed by a baghouse are provided for cooling and cleaning of the exhaust gas. The gas is continuously sampled from the cyclone exit through a Pall filter cartridge, refrigerated to -10 C, reheated trough a Purma-pure dryer and analysed by a Beckman model 755 Oxygen analyser, Infared Industries model IR-702 CO/CO2 analyser, and a Western Research model 721A SO2 analyser.



1 Feed hopper
2 Thermocouples
3 Monometer
4 4 Pairs resistance heaters
5 316 Stainless tube
6 Porous quartz distributor
7 Preheated packing
8 Cyclone
9 Purmapure filter and dryer
10 Beckman 865 SO_2 analyser
11 Sample receiver
12 Ball valve
13 Filter
14 Vacuum pump
15 Vacuum reservoir
16 Flowmeters
17 Electronic mass flow controller
18 Electronic mass flow meter
19 Heater tape

Fig. 1. Fluidized bed reactor



1-pneumatic feed
2-fluidizing air
3-windbox
4-distributor
5-150 mm tube
6-electric heater
7-sight port
8-propane burner
9-100 mm ceramic tube
in castable insulation
10-cyclone
11-quartz sight tube
12-air ejector
13-exhause to heat exhanger
and bag house

Fig. 2. Pilot-scale circulating fluidized bed combustor

RESULTS AND DISCUSSION

Sulphation Capacity of Coarse Particles

The FBR method was designed for evaluating limestones for use as SO2 sorbents in bubbling AFBC systems. The particle size for the test was defined as 850 - 1000 um as this represents a medium size for this type of fluidized bed combustor. The sulphation capacity of all the NB sorbents evaluated in this size range is given in Table 4 according to the FBR and chemical analysis data.

Table 4. Sulphation capacity of NB sorbents, 850 - 1000 um

Sample	Sulphation capacity			
	FBR	Chem analysis	mean	dev %
NB-1-12	29.0	-	-	-
1-13	30.7	34.5	32.6	5.8
2	25.3	25.1	25.2	0.4
3	26.7	27.6	27.2	1.7
4	19.1	-	-	-
4-2	18.9*	23.8	21.4	11.5
4-3	22.8*	29.5	26.2	12.8
5	25.9	-	-	-
6	27.2	39.7	33.5	18.7
7	21.9	-	-	-

* Average of two tests

According to the FBR data the two samples from Havelock appear to be the best sorbents from New Brunswick in this size range. The sulphation capacities of a dozen limestone samples from this source over the past six years have ranged from 27 to 34% with the average being 30.3%. There appears to be little difference between limestone from the two quarries serving the Havelock plant. The samples from Elmtree Petit Rocher quarry appear to be the poorest sorbents closely followed by the Markhamville limestone and the Elmtree Sormony quarry. Except for NB-6, the sulphation capacity determined from the chemical analysis of S and Ca agree with the FBR results within 13 %. It should be noted that in earlier test work on a number of sorbents in the 850 - 1000 um size the sulphation capacity as determined by the FBR and chemical analysis normally agreed within 5 - 10 %.

Sulphation Capacity of Finer Particles

The intent in testing the seven size fractions listed in Table 2 was to determine the effect of particle size on sulphation capacity. The following Table 5 gives the sulphation capacity for the various size fractions as determined by the FBR.

Table 5. Sulphation capacity versus particle size, FBR

Sample (Mesh)	Size Range 16*20	20*28	28*48	48*65	65*100	100*200	200*325
Ave dia,um	925	722	447	256	181	112	60
NB 1-12	29.0	30.0	28.4	31.4	35.4	32.6	37.0
1-13	30.8	35.5	35.0	38.2	39.8	46.6	45.1
6	27.2	-	29.7	-	-	-	37.3
7	21.9	24.9	25.4	-	27.1	-	31.8
4-2	18.9*	18.2	19.6	20.3*	20.3	25.4	32.6
4-3	22.9*	23.4*	25.1	20.3	22.2	24.1	31.8

* average of 2 tests

The data for the Havelock and Elmtree quarries is graphed on a semi-log scale in Figure 3. The data for NB-6 and 7 are incomplete and, as these deposits were not deemed to be potential sources of limestone for the Chatham CFBC, are not included on the graph. Only with the Havelock samples does the sulphation capacity appear to increase exponentially with decreasing particle size. With the other samples the sulphation capacity does not appear to change significantly between the 850 - 1000 um and the 212 - 300 um fraction after which it increases with the finer fractions.

As a further check on the results of the Elmtree material, the sample of NB-4-2, which was labled as agricultural limestone, was tested as plus 300 um coarse material and as pellets of minus 300 um fine material. The pellets made from the -300 um limestone should be stronger than those made from the narrower size range material. The sulphation capacity of the +300 um was 21.0% and of the pelletized -300 um material was 26.0%. Both results are in reasonable agreement with the other tests on this limestone.

Chemical Analysis of Sulphated Limestone

After the FBR tests the bed material of sand and sulphated limestone was recovered via a vacuum system into a collection receiver. By sieving and hand sorting, samples of the sulphated limestone were recovered for chemical analysis of calcium and sulphur. The per cent sulphation of the lime calculated from the analysis are generally in fair agreement with the results obtained from the FBR. A graph of the Havelock samples by the two methods is given as Figure 4 and of the Elmtree samples as Figure 5. Figure 4 indicates a much higher suphation capacity determined by the chemical analysis than by the FBR, especially with the finer size fractions. By the chemical analysis the sulphation capacity of the finer sizes is in the 55 - 60 % range compared to the 35 - 45 % by the FBR. This may partially be explained by the attrition and loss of incompletely reacted material, especially from the pellets, which would tend to result in lower sulphation capacities for the FBR method. Pellets made with closely sized particles are inherently weaker than those made with a large size range distribution where the varying sizes of particles allows closer packing and filling of voids between particles.

The sulphation capacity calculated from the chemical analysis and plotted in Figure 5 show a considerable degree of scatter such that drawing a line through the points was not

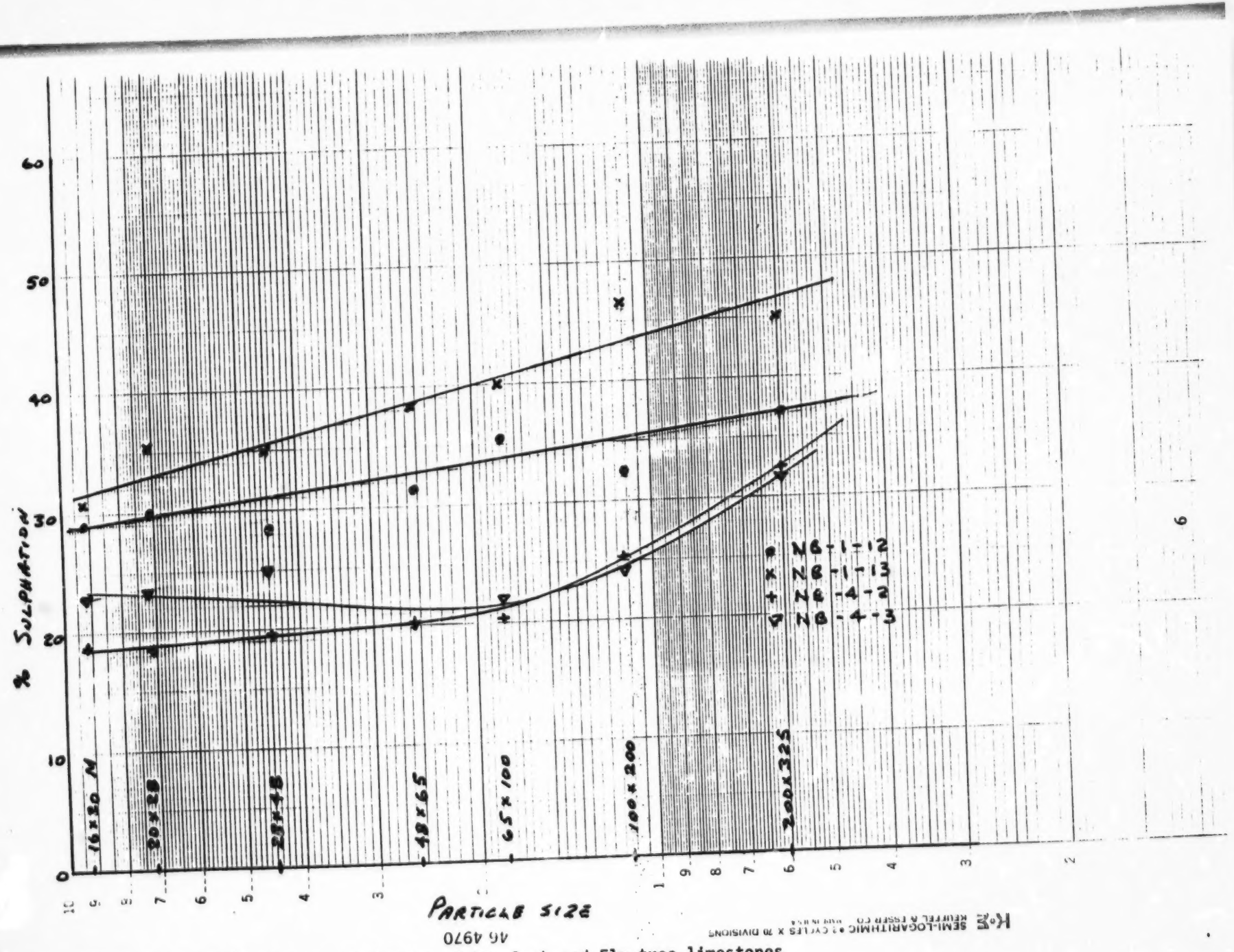


Fig. 3. Effect of particle size on sulphation of Havelock and Elm tree limestones

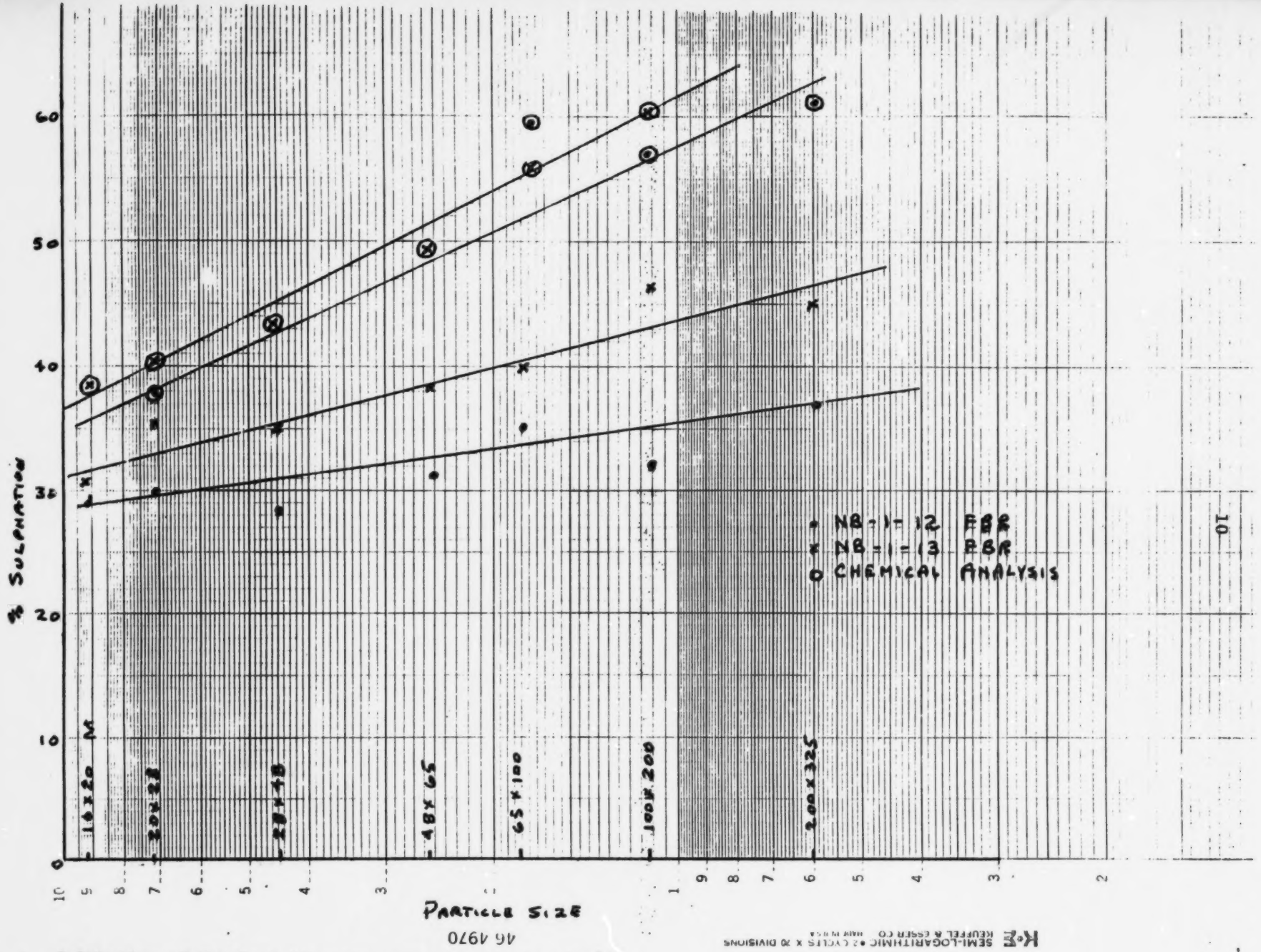


Fig. 4. Sulphation of Havelock limestone versus particle size as determined by the FBR and chemical analysis

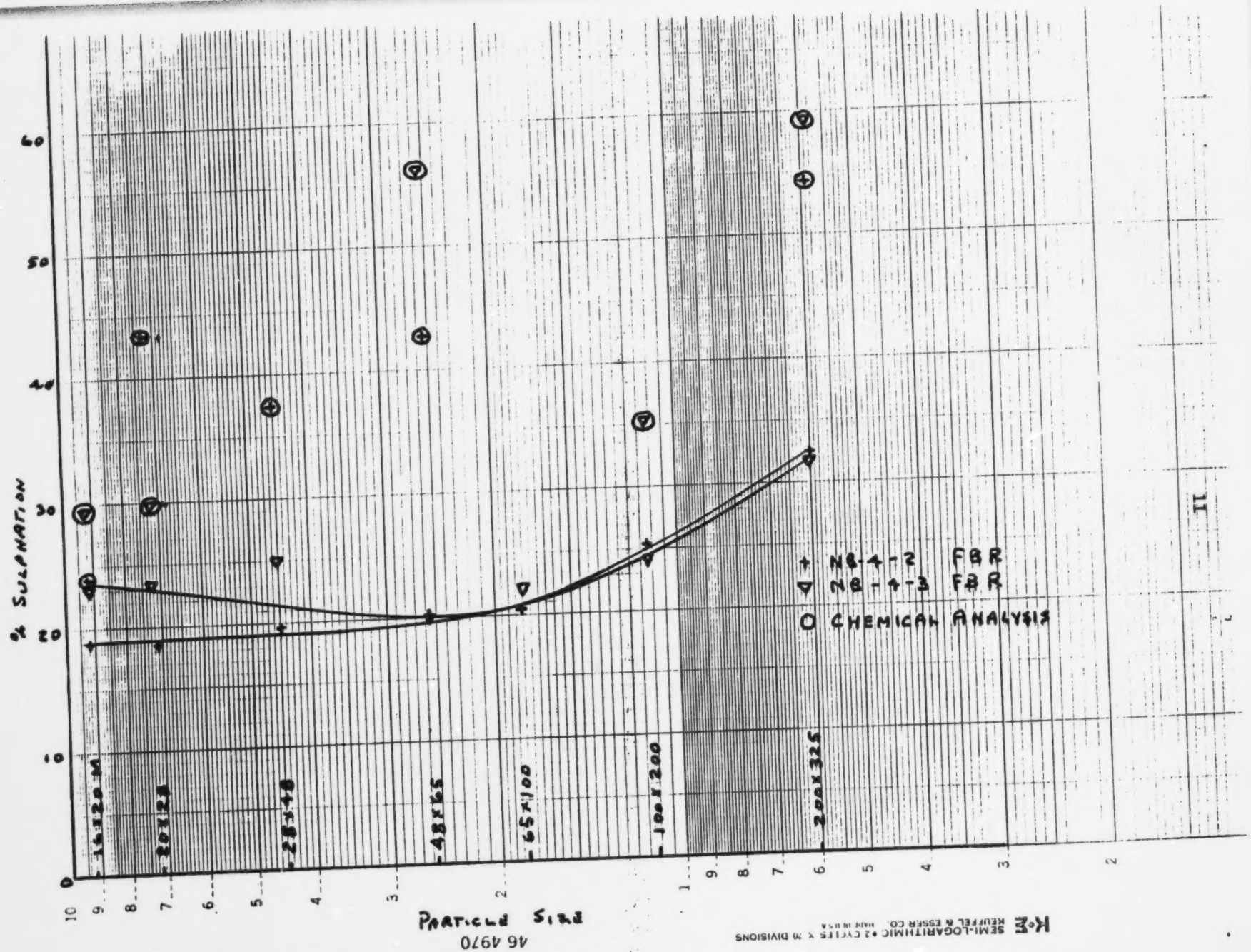


Fig. 5. Sulphation of Elm tree limestone versus particle size as determined by the FGR and chemical analysis

feasible. This scatter brings into question the accuracy of some of these results.

The conflicting results from the two methods of determining sulphation capacity cause some difficulty in predicting the behaviour of these limestones for CFBC use. The sulphation of the limestones which would be achieved in a CFBC probably lie between the results of the two methods, that is, the sulphation determined from the chemical analysis is too high and that from the FBR is too low, especially with the pelletized samples.

Sulphation Capacity of the Marl

Samples of the marl, after drying and sieving to recover "natural" pellets were tested in the FBR. Immediately after injecting the sample into the reactor the SO2 in the exhaust gas decreased to almost zero. This extreme decrease in SO2 has never been observed to the same extent with any other sample tested. The marl sulphated much more rapidly than normal limestones and gave a sulphation capacity of 25 and 33 % for two tests. Very little sample was recovered from the bed material at the end of the test indicating that most of it had been elutriated from the reactor.

A sample of the fine marl was pelletized with bentonite as a binder. Two tests of these pellets resulted in sulphation capacities of 76 and 72 %. These high results attest that this marl is an extremely reactive SO2 sorbent.

Pilot-scale CFBC Test of Marl

The size distribution of the marl is much finer than is normally used in CFBC. To determine how this material would behave a test run was conducted in MSL's pilot-scale CFBC. There was suffient marl for only one combustor trial of relatively short duration. Syncrude coke with 6.9 % S was blended with marl in a Ca/S ratio of 1.75. The initial bed material, 7 kg, was a mixture of partially sulphated limestone, ash and sand from previous combustion trials with the same fuel and Fort McMurray limestone. The combustor was run for five hours with a feed rate of 4.75 kg/h blended feed. The fluidizing gas velocity was 3 m/s and the combustor temperature over the last 3 1/2 h was 870 +10-20 C.

At the end of the run the solids from the bag house, heat exchanger and bed were drained and weighed. Samples of the first two streams were analysed by thermogravimetric analysis for unreacted carbon and calcium carbonate. The results are in Table 6

Table 6. Material balance of marl test run

In		Out		Analysis
Old bed	7000 kg	Bed	5890	
Feed	23600	Heat ex	4039	22.2% C, 7.4% CaCO3
		Bag H	3003	5.0% C, 13.7% CaCO3

There was a loss of bed material during the run since the ash from the coke is very fine and does not stay in the bed and the marl was also too fine to be retained. The carbon content of the heat exchanger is double that which is usually observed with this

fuel, however this test was run with only 5 % excess air. The carbon content in the bag house material is normal. The bed was not analysed but normally contains very little carbon. Based on the analysis, the combustion efficiency was only 89.6 %. The unreacted limestone in the heat exchanger and bag house is less than was expected. It is in fact similar to the results with Fort McMurray limestone which had a much coarser size distribution.

Although the particle size of the marl is so fine that probably little of it was recycled by the cyclone there was appreciable SO2 capture. Based on gas analysis the theoretical SO2 would have been 5600 ppm with no sulphur capture. The average SO2 emission over the last 3 1/2 h of the 5 h run was 1120 ppm and 930 ppm over the last hour of the run. This translates to a calculated SO2 retention of 80 - 83 %. This SO2 capture is better than was anticipated considering that much of the material probably had a short residence time in the combustor. The gas residence time for the pilot-scale CFBC is about one second. For the Chatham CFBC which is about 30 m high and has a gas residence time of about 4 seconds, the SO2 retention should be considerably improved over these test results.

CONCLUSION

An attempt was made to evaluate New Brunswick limestones for use as SO2 sorbents in the CFBC at Chatham. Samples submitted by NBEPC were tested in various size fractions in a bench-scale fluidized bed reactor to determine their sulphation capacity. Most of the sulphated limestones were analysed chemically for Ca and S and the % sulphation calculated from the analysis. Unfortunately the results of the two methods were in only fair agreement, the chemical technique giving much higher sulphation capacities than the FBR, particularly with the finer size fractions. Based upon the FBR results the limestones from Havelock perform better than those from Elmtree. Ignoring some of the scatter in the chemical data, it too indicates a preference for Havelock except perhaps in the very smallest size ranges. The sample from Glebe Mine appeared similar to that from Samphill.

Because of the difficulty in evaluating the finer sized material in the FBR, it is recommended that these samples be tested by TGA. There is no need to pelletize fine samples as there is no loss of material from the TGA.

Alternatively, the limestones can be evaluated in combustion trials in a pilot-scale CFBC as was done with the marl sample. Although the particle size distribution of this material is much finer than normally used in CFBCs, reasonable SO2 capture was achieved, 80 % at a Ca/S ratio of 1.75, in a short duration test. Even though its size distribution may preclude this material from use in the CFBC, it should be considered for use in lime injection (LIMB) process.

ACKNOWLEDGEMENTS

The FBR tests were done by G. Davidson and the chemical analysis of those samples by J.C. Hole's Ore and Fire Assay Section. The operation of the pilot CFBC was by D.T. Liang and J. Kearns. TGA analysis was by S.A. Mikhail.

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